

[19] Japanese Patent Office (JP)
[12] Patent Disclosure Bulletin (A)
[11] Patent Disclosure No.: Sho ⁸⁶~~61~~-242561
[43] Disclosure Date: October 28, 1986
[51] Int. Cl.⁴: A 23 L 1/304

Identification Code:

Interagency Reference No.: 7110-4B

Request for Review: not submitted

Number of Inventions: 1

(Total 6 pages)

[21] Patent Application No.: Sho 60-84384

[22] Application Date: April 22, 1985

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[54] Title: FOOD ADDITIVE

Specification

1. Title

FOOD ADDITIVE

2. Claims

A food additive characterized by the fact that it contains an aluminosilicate represented by the general formula $(1.0 \pm 0.2)M_{2/m}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ (where M represents an alkali metal, an alkaline earth metal, iron, copper or cobalt, m represents the valence, x is 1.5-5, and y is 0-10) as an effective component having its basicity adjusted so that the equilibrium pH is 10 or lower.

2. A food additive as described in Claim 1, wherein the aluminosilicate used is an amorphous fine particulate zeolite precursor.

3. A food additive as described in Claim 1, wherein the aluminosilicate used is selected from among zeolite A, P, X and Y.

4. A food additive as described in Claim 1, wherein the aluminosilicate used is a calcium-substituted aluminosilicate.

3. Detailed Description of the Invention

Field of Industrial Application

The present invention relates to a food additive that contains an aluminosilicate having an adjusted basicity as an effective component and can be used for various types of food.

Prior Art

The diversification of modern everyday life is accompanied by a diversification in the kinds of food consumed. In food processing, safer food additives are required in order to accommodate changes in the required distribution system and storage performance.

Aluminosilicates are known as food additives. For example, an

aluminosilicate produced by a special method is used as an anti-lumping agent for sodium chloride, and is also used as a medicine for its antacid action.

However, it is extremely limited in its use, and is virtually unknown as a food additive in Japan.

Problems to be Solved by the Invention

The reason why aluminosilicates are not commonly used are as follows: Natural aluminosilicates are extremely stable, physiologically inactive, and have almost no action during food processing. On the other hand, synthetic zeolites have extremely high basicity.

Therefore, only the conventional synthetic zeolite obtained by reacting aluminum sulfate with sodium silicate or soluble calcium salt as needed under special conditions is used in very small amounts.

Solution to the Problem

In view of the above, the inventors investigated the function of aluminosilicate and discovered that a certain type of synthetic zeolite or a precursor thereof had better performance as a food additive than the conventional aluminosilicate and could be used in place of known calcium carbonate, calcium chloride, calcium oxide, etc or along with these compounds; the invention is based on this discovery.

Thus, the invention proposes food additives characterized by the fact that they contain aluminosilicate represented by the general formula $(1.0 \pm 0.2)M_{2/m}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ (where M represents an alkali metal such as potassium, sodium, lithium, etc, an alkaline earth metal such as calcium, magnesium, etc, iron, copper or cobalt, m represents the valence, x is 1.5-5,

and y is 0-10) as an effective component having its basicity adjusted so that the equilibrium pH is 10 or lower.

The aluminosilicate used in this invention may be amorphous or crystalline. A crystalline aluminosilicate is generally called zeolite, which has a unique three-dimensional crystal structure with molecular sieve-like pores.

The crystalline aluminosilicates used in this invention include zeolite A, zeolite P, zeolite X and zeolite Y. The amorphous aluminosilicates include precursors of the above-listed crystalline aluminosilicates.

The above-specified zeolite or its precursor is generally sodium aluminosilicate, regardless of its crystallinity, and also includes substituted aluminosilicates in which the sodium is substituted by one or more of the above-mentioned metals.

Of the above-mentioned aluminosilicates, zeolite A and its precursor, amorphous aluminosilicate, are industrially suitable.

Production methods for the above-mentioned aluminosilicates are known in most cases, and their production history is not restricted.

For example, an amorphous gel of sodium aluminosilicate, which is a precursor of zeolite, is obtained by reacting a specific ratio of aqueous sodium aluminate solution and aqueous sodium silicate solution, and is converted to crystalline zeolite by heating and aging. Furthermore, a metal-substituted aluminosilicate is obtained by bringing the above-mentioned amorphous aluminosilicate gel or zeolite in the form of an aqueous slurry into contact with a soluble salt of the substituent metals. Examples of substituent metals are alkali metals such as potassium, sodium, lithium, etc,

alkaline earth metals such as calcium, magnesium, etc, iron, copper and cobalt; calcium aluminosilicate is particularly suitable.

The food additive of this invention must have its basicity adjusted so that the equilibrium pH is 10 or lower, preferably 9.5-5, in all cases of the above-mentioned aluminosilicates.

The reasons for adjusting the basicity are as follows. Unlike other soluble sodium salts, sodium aluminosilicate gradually releases cations; it has mild, sustained basicity. When this substance is ingested, alkalosis of bodily fluid occurs; this condition must be prevented. When the basicity is too low, the physical properties of aluminosilicate deteriorate, and its antacid action is reduced.

The basicity is adjusted by thoroughly washing the above-described aqueous aluminosilicate slurry with water or by neutralizing it with a suitable acidic substance. Examples of acidic substances are inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, carbonic acid, etc and organic acids such as monocarboxylic acids like acetic acid, butyric acid, propionic acid, etc, dicarboxylic acids like oxalic acid, fumaric acid, malonic acid, succinic acid, etc, and oxycarboxylic acids like glycolic acid, lactic acid, malic acid, tartaric acid, citric acid, gluconic acid, etc, but the choice is not limited to these examples.

The food additive of this invention is not limited to the above-specified aluminosilicate itself; it includes physical or chemical adducts of aluminosilicates with the salts used for the neutralization or adjustment of basicity and aluminosilicates carrying physiological microelements, ie, minerals utilizing the adsorptivity of aluminosilicate.

The term "equilibrium pH" as used herein is the pH of an aqueous slurry containing 5 g of aluminosilicate sample per 100 mL measured after stirring at 25°C for 30 min.

The aluminosilicate of this invention is prepared from conventional sodium silicate and aluminum sulfate, magnesium sulfate, etc as starting materials, and is known as an antacid. Its physical properties differ markedly from those of other aluminosilicates. This aluminosilicate itself is neutral or weakly alkaline, has an ion exchange capacity and gradually releases cations such as sodium, calcium, magnesium, etc when it comes in contact with an acid; thus it has a buffer effect and gradually neutralizes acids; in particular, an excellent antacid action is maintained at pH 5-3.

The pH curves of slurries of food additives of this invention and calcium carbonate, etc obtained by titrating with hydrochloric acid are shown in the attached diagram. The diagram shows calcium carbonate (1) used as a food additive (commercial product), amorphous sodium aluminosilicate (2), sodium zeolite A (3), amorphous calcium aluminosilicate (4) and calcium zeolite A (5).

As described above, the aluminosilicates of this invention have a stronger buffer action than calcium carbonate, and have a characteristic mineral releasing effect.

The above-reported test results were obtained by the following procedure.

The change in the pH is measured by adding 0.1 N HCl at the rate of 1 cc/min at $37^{\circ}\text{C} \pm 1^{\circ}\text{C}$ to 50 mL of suspension containing 0.5 g of sample.

In the case of aluminosilicates substituted with calcium, magnesium, copper, iron, cobalt, etc, the above-mentioned cations are gradually released;

in contradistinction to the calcium sources or mineral sources of conventional food additives, not only are an antacid action and an intestinal function controlling action observed, but the cations are gradually absorbed in the body as a supply source of calcium and minerals; physiologically this is extremely desirable. The copper-substituted aluminosilicate has prolonged bacteriocidal action and is effective as a food preservative.

The aluminosilicate of this invention is in the form of fine particles and has surface activity. Zeolites also have unique pores of 3-13 Å diameter due to their crystalline structure, and because of their excellent absorptive power, are suitable as supports for various food additives such as preservatives, artificial sweeteners, colorants, emulsifiers, reinforcing agents, antioxidants, pigments, stabilizers, etc or are diluents; they can be effectively used as composite food additives. Particularly, calcium aluminosilicate can be used in place of or with calcium carbonate, and is effective for the calcium enrichment of various processed agricultural foods, processed seafoods, processed meats and confections.

In the case of chewing gum, calcium carbonate and talc are blended in order to adjust the hardness, elasticity, viscosity or film forming property of the gum base. When the aluminosilicate of this invention is used instead of calcium carbonate or talc, an anticariogenic effect is exhibited as well as the above-mentioned effects.

Generally, the major causes of dental caries are considered to be the adhesion of polysaccharides to the teeth and the dissolving of the apatite in the dentin by organic acids such as lactic acid, pyruvic acid, etc produced by the decomposition of polysaccharide by the action of bacteria in the oral

cavity.

In the case of chewing gum blended with the aluminosilicate of this invention, eg, calcium aluminosilicate, organic acids produced by the action of oral bacteria are neutralized by the antacid action with a strong buffer action in the chewing process, thus preventing dental caries.

The addition of the product to other foods has similar effects. When the food additive of the invention is added to confections, it fortifies nutritionally as a calcium source, and confections can be offered as health foods having an anticariogenic effects.

The food additive of this invention has the unique effect of adsorbing and desorbing water, and can act as an anti-lumping agent for processed foods when used with a glycerol fatty ester as needed.

The amount of food additive of this invention used varies depending on the type and physical properties of the aluminosilicate, the type of food and the purpose of the addition, but is generally less than 10 weight percent, preferably less than 3 weight percent.

Actual Examples

This invention is described in further detail in actual examples (subsequently referred to simply as "example"). The term "part" used in the examples refers to weight parts unless otherwise stated.

Sample Preparation Example

An aqueous sodium silicate solution (Na_2O : 8.1 weight percent, SiO_2 : 6.6 weight percent) and an aqueous sodium aluminate solution (Na_2O : 9.3 weight percent, Al_2O_3 : 5.6 weight percent) at a molar ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of

2.0 were mixed at 60°C, yielding a gel-like reaction product.

Subsequently, the gel-like substance was crystallized by thermal aging, yielding sodium zeolite A.

Using the gel-like reaction product (amorphous aluminosilicate) obtained as reported above and sodium zeolite A, a 200 g/L slurry of each was prepared. Each slurry was reacted with a 100 g CaCl₂/L calcium chloride solution for adequate ion exchange, and the calcium-substituted amorphous aluminosilicate and calcium zeolite A obtained were separately washed with water and neutralized with a citric acid solution, yielding calcium-substituted amorphous aluminosilicate (sample 9) and calcium zeolite A (sample 2). Sample 2 was heated at 400°C for 2 hr, yielding anhydrous calcium zeolite A (sample 3). The chemical composition and physical properties of each sample are shown in Table 1.

Test Example

DTJ medium containing 2% of glucose (medium A), DTJ medium containing 2% of sample 1 (medium B) and DTJ medium containing 2% of sample 2 (medium C) were prepared, and 10 mL each was placed separately in a test tube and sterilized.

0.1 mL each of a typical cariogenic oral bacterium was inoculated in each medium and cultured at $36.5 \pm 0.5^\circ\text{C}$; the formation of organic acid in each medium after a certain period of time was determined by titrating with 0.1 N NaOH solution. The results are shown in Table 2.

As evident from the results in Table 2, the food additives of this invention have the effect of completely neutralizing the organic acid produced by cariogenic bacteria, and the anticariogenic effect is evident.

Table 1.

	Sample 1	Sample 2	Sample 3
Na ₂ O	5.1	4.4	5.6
CaO	11.5	11.5	14.6
Al ₂ O ₃	29.1	28.2	35.7
SiO ₂	37.8	33.2	42.1
H ₂ O	16.8	22.7	2.0
X-ray diffraction	amorphous	zeolite A	zeolite A
Equilibrium pH	8.5	8.7	8.5

Table 2. (units: mL)

Bacterium	S. mitis			S. bovis			L. fevmenti		
Medium	A	B	C	A	B	C	A	B	C
Time									
6	0.31	0	0	1.35	0	0	1.68	0	0
12	2.25	0	0	4.80	0	0	4.70	0	0
24	4.15	0	0	7.45	0	0	7.08	0	0

Example 1

80 parts polyvinyl acetate, 40 parts ester gum, 3 parts butyl phthalate, 15 parts natural chicle, 6 parts stearyl monoglyceride and 10 parts sample 2 (calcium zeolite A) were placed in a kneader and blended while heating, yielding a chewing gum base.

To the chewing gum base obtained, 250 parts granulated sugar, 100 parts

crystalline glucose, 80 parts honey, and suitable amounts of flavoring and colorant were added; the mixture was roll blended and formed into a plate, yielding chewing gum sticks.

Chewing gums obtained were tested by 20 panelists, and the chewing features such as feel on the teeth, feel on the tongue, etc were found to be comparable to those of conventional chewing gums.

The chewing gum of this invention having an anticariogenic effect is healthier than conventional chewing gums, as substantiated by the results in Table 2.

Example 2

According to a procedure similar to that described in Example 1, a chewing gum was prepared using sample 1 (amorphous calcium aluminosilicate) instead of sample 2.

The chewing gum obtained had chewing qualities similar to those of Example 1.

Example 3

80 parts polyvinyl acetate, 40 parts ester gum, 15 parts natural chicle, 3 parts sorbitan monostearate and 3 parts butyl phthalate were placed in a kneader and blended, yielding a chewing gum base.

To the chewing gum base obtained, 250 parts granulated sugar, 100 parts crystalline glucose, 80 parts honey, 30 parts thick malt syrup and suitable amounts of flavoring and colorant were added; the mixture was blended and formed according to a common procedure.

Separately, 100 parts of sample 3 (anhydrous calcium zeolite A) and 100

parts stearyl monoglyceride were blended while heating, cooled, and made into a powder having an average particle size of 100 microns, which was used as a release agent for chewing gums.

To test the release properties, the above release agent was thinly coated on the surface of a 17 cm x 10 cm x 1 cm sample gum block, and the block was passed between rollers having a 5 mm nip to investigate the degree of sticking to rollers.

In order to investigate the storage properties, 10 samples of completely packaged product were left standing in a thermostatted chamber at 30°C and 80% relative humidity for three weeks; the adhesion to and release from the inner wrapping were examined, and changes in product quality features were examined organoleptically.

The test results indicated that the product had excellent release properties, without sticking to the apparatus, etc, as well as good lubricity and workability. After three weeks of storage, the gum did not adhere to the inner wrapping, released readily and exhibited no bad taste or malodor; with regard to these features, no differences were observed from the product before storage. For the sake of comparison, a release agent containing no sample 3 was used. Both the molding properties and the storage properties were inferior.

Example 4

100 parts wheat flour, 40 parts sugar, 20 parts oils/fats, 10 parts egg, 10 parts powdered skim milk, 5 parts thick malt syrup and 3.5 parts sample 2 (calcium zeolite A) were mixed, together with a suitable amount of water.

The dough obtained was shaped into a disk and baked at a temperature of

120-300°C, yielding biscuits.

The chewing qualities such as the feel on the teeth and tongue were excellent, and the biscuits were tasty.

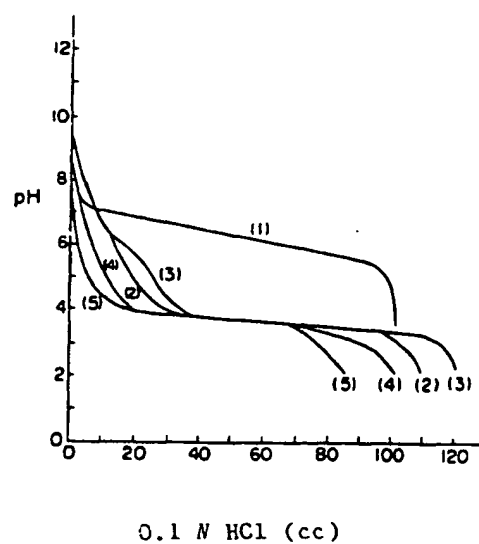
As evident from the results in Table 2, the biscuits obtained qualify as a health food with an anticariogenic effect.

Effect of the Invention

The food additives of this invention have the merit of producing health foods having anticariogenic effects, and the feel on teeth and tongue are comparable to those of conventional food additives.

4. Brief Description of the Diagrams

The diagram shows changes in the pH of commercial calcium carbonate and aluminosilicate food additives of this invention titrated with hydrochloric acid. In the diagram, (1): calcium carbonate as food additive (commercial product), (2): amorphous sodium aluminosilicate, (3): sodium zeolite A, (4): amorphous calcium aluminosilicate, and (5): calcium zeolite A.



PATENTS SUMMARY

04/23/99

Page 1

Country : Japan

Patent #: 86-242561 A

Index#: 2543

Inventor: Muneo Mita et. al.

Issue Date: 10/28/86

Assignee: Nippon Kagaku

Date of Application: 04/22/85

Title:

FOOD ADDITIVE

Japan A Patent

Desc.:

An especially prepared aluminosilicate with pH adjustment is used as a food additive. When used in chewing gum instead of calcium carbonate or talc, an anticariogenic effect is obtained. It is also an antacid, good source of calcium, a food preservative, an absorptive support for food additives and an anti-lumping agent.

Key Words:

10 CHEWING GUM
20 Anticaries/Antiplaque (Gum)
25 Pharmaceutical
460 Acids/Buffers/pH
461 Salt, Ions, Metals, Minerals
525 Chemical Synthesis/Preparation
556 Shelf Life/Stability
574 Health Benefit
600 ORAL HEALTH
601 Anticaries/Antiplaque/Anticalculus
799 Other Company/Institution
803 Japan